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ART. XII.—*Studies in the Physical Chemistry of Essential Oils.*

PART I.—*The Physical Properties of mixtures of two Terpene substances in relation to those of the constituents.*

BY

R. BARRY DREW, M.Sc.,

AND

E. IVAN ROSENBLUM, M.Sc.

(Communicated by W. Heber Green).

[Read 9th July, 1914).

It is of considerable interest to regard the mixture of organic bodies which is presented to us by an essential oil from a physicochemical, as well as from the ordinary systematic point of view. We have here a class of mixtures, easily obtained in quantity, whose constituents are mostly well-known, and of allied structure; conditions which suggest a novel method of attacking the general theory of solution, and should also give us valuable data for judging the general composition of an oil from its physical constants —a problem of interest, both from the commercial and from the scientific standpoint.

As showing the questions which meet us here we may cite as an instance two eucalyptus oils from the same species, which yielded the same percentage of phellandrene $[\alpha = -69^\circ]$ and contained no other optically active substance, whose rotations were as far distinct as -23° and -44° respectively.

The major portion of an essential oil usually consists of one or more terpenes. These may be considered as simple examples of non-ionising, unassociated solvents, and it will be well, therefore, to start our inquiry into essential oil equilibria by the study of these simple substances, adding progressively more complex or more reactive constituents, such as oxygenated derivatives, etc., and essaying to evaluate the new solution factors as they occur.

An ideal investigation, then, would start from the simplest case—a mixture of two terpenes—proceed through increasing complexity in the number and nature of the components, and finally reach that complicated equilibrium presented by a natural essential oil, such as that of Eucalyptus globulus.

The following results are of a preliminary nature, and are concerned with the simpler cases of such an inquiry.

Experimental.

The method followed in the measurements here recorded was to make mixtures of various concentrations from materials prepared as freshly as possible. The density. refractive index, and rotation of these were taken at 25° C., with such methods and precautions as accurate physicochemical work suggests.

The pyknometer held about 6 c.c's., and the temperature adjustment was correct to .01°. The rotations were taken in a 100 mm. tube in a Schmidt and Haensch polarimeter, and the refractive indices in a Zeiss refractometer, and for each of these the divergence in temperature did not exceed .1°.

The mixtures themselves were made up by successive additions of one constituent to a definite amount of the other—a method economical of material—and the results have shown it to be justified, for any systematic error arising from this cause would increase with each addition, and such increases have not appeared.

Calculation of Results.

We may comment here on the methods employed for calculating the theoretical value of any physical property of a liquid mixture. If the property under consideration is additive, and no anomaly is present, we have—

$$P_{(\text{calc.})} = \frac{m_1 P_1 + m_2 P_2}{m_1 + m_2}$$

where P_1, P_2, are the values of the property considered, for the individual substances, and m_1 and m_2 are the masses of these substances in the mixture. If the additive relationship does not hold, however, we must modify the formula to express the effects of the molecules, atoms or ions, which are the disturbing factor. Thus, if the molecules are the reacting entities to be considered, we have [M_1, M_2 being the molecular weights]—

$$P_{(\text{calc.})} = \frac{\frac{m_1 P_1}{M_1} + \frac{m_2 P_2}{M_2}}{\frac{m_2}{M_1} + \frac{m_2}{M_2}}$$

Since many factors in liquid mixtures are influencing a particular property, it is necessary to introduce more and more terms before we can attain concordance. But since the difficulty of interpreting the equations so obtained, makes this rather a waste of labour, it suffices at present, where properties are atomic (*e.g.*, Refractivity) to use the first of these equations, while for those where the molecular influence is introduced (*e.g.*, Density) the second formula, giving what is known as the Molar Fraction, serves as some correction.

Hence, these two methods of calculation are all that have been employed in the present research.

The System l-pinene—d-pinene.

In considering the purity of the terpenes mentioned, it must be remembered that where suitable solid derivatives, from which a terpene may be regenerated in quantity, are wanting, the only means of purification is repeatedly to distil under diminished pressure. The product, of course, may be partly racemised, or may contain some of its optical isomers. For this reason the physical properties of two optical isomers, such as d- and l-pinene, are not numerically identical, a point which is of little significance in the present research, since these well-fractionated terpenes are "pure" from the practical point of view. Indeed, the l-pinene of rotation −39° is almost free from racemate, while the + 25° rotation of the d-pinene is quite as high as other workers have usually obtained. In the mixture of these two isomers, from our standpoint, the simplest case, we should anticipate no constitutive effects, and indeed, the observed properties of the mixtures agree excellently with those calculated by (1), the simple mixture formula, and the slight deviations which occur may be taken as indicative of the magnitude of the experimental error in the other systems as well.

The pinenes were obtained from oils from Eucalyptus dextro pinea and E. laevopinea, which were generously given us by Mr. Smith, of the Sydney Technological Museum. He has worked out their composition, and his results we have confirmed, and by distilling in a rod and disk apparatus at 10 mm. pressure we have obtained pinene fractions with the following properties:—

At 25°C.	d-Pinene.	l-Pinene.
Rotation ...	+25.40°	−39.64°
Refractive Index	1.4640	1.4639
Density ...	.8604	.8646

THE SYSTEM D-PINENE—L-PINENE.

l-pinene Concentration	l-pinene.	A.	B.	C.	D.	E.	d-pinene.
	100	86.82	75.04	50.87	28.98	15.92	0
Rotation—							
Found ...	−39.64°	−31.39°	−23.60°	−7.80°	+6.45°	+15.02°	+25.40°
Calc. ...	...	−31.37°	−23.66°	−7.83°	+6.51°	+15.05°	...
Refractive Index—							
Found ...	1.4639	1.4641	1.4640	1.4640	1.4641	1.4640	1.4640
Calc. ...	...	1.4640	1.4640	1.4640	1.4640	1.4640	...
Density—							
Found ...	.8646	.8639	.8633	.8626	.8614	.8610	.8604
Calc. ...	...	.8640	.8636	.8625	.8616	.8611	...

The Systems l-Pinene-Cineol and d-Pinene-Cineol.

Of greater complexity is the case involving a partial replacement of one of the terpenes by an oxygenated substance of allied structure. Cineol is such a substance, and with it the deviations from the simple proportionately become noticeable.

These deviations, as in the case of the specific rotatory power, may be due to a disturbance of the equilibrium, between active and racemic terpene, brought about by the cineol, a possibility supported by the fact that the refractivity is not affected.

It is in the density, however, that the divergences from the simple proportionality become most marked, and here it can be shown that the influence is molecular rather than structural, by the fact, that when the theoretical densities are calculated from the molar fractions they again agree with the observed. In the simpler case of d- and l-pinene the molar and weight fractions, of course, coincide, since the two molecular weights are the same.

The cineol was obtained from Bosisto's Ol. Eucalyptus B.P. by conversion into the phosphoric acid compound and regeneration with soda, after squeezing out the terpenes under pressure. The product was then distilled with steam, and its constants were—

$$\alpha = \pm 0.00^\circ$$
$$\mu_{25} = 1.4579$$
$$\delta_{25} = .9220$$

THE SYSTEM L-PINENE—CINEOL.

	l-pinene.	A.	B.	C.	D.	E.	cineol.
Concentration l-pinene.							
Mol. p.c. ...	100	82.46	51.36	36.26	16.34	11.69	0
Wt. p.c. ...	100	80.26	48.24	33.44	14.71	10.47	0
Rotation—							
Found ...	−39.64°	−32.38°	−19.65°	−13.67°	−5.98°	−4.25°	0°
Wt. p.c. ...	...	−32.13°	−19.31°	−13.38°	−5.89°	−4.19°	...
Mol. p.c. ...	...	−33.00°	−20.56°	−14.51°	−6.54°	−4.67°	...
Refractive Index—							
Found ...	1.4639	1.4629	1.4608	1.4600	1.4587	1.4585	1.4579
Wt. p.c. ...	...	1.4628	1.4608	1.4600	1.4588	1.4585	...
Density—							
Found ...	.8646	.8751	.8931	.9016	.9128	.9166	.9220
Wt. p.c. ...	...	.8760	.8944	.9029	.9136	.9169	...
Mol.p.c. ...	...	.8747	.8936	.9012	.9127	.9164	...

THE SYSTEM D-PINENE—CINEOL.

	d-pinene.	A.	B.	C.	D.	E.	cineol.
Concentration d-pinene—							
Wt. p.c. ...	100	82.84	64.18	46.85	30.12	17.91	0
Mol. p.c. ...	100	84.54	66.98	49.95	32.80	19.81	0
Rotation—							
Found ...	25.40°	21.22°	16.56°	12.07°	7.78°	4.60°	0°
Wt. p.c. ...	...	21.04°	16.30°	11.90°	7.65°	4.55°	...
Refractive Index—							
Found ...	1.4640	1.4630	1.4618	1.4609	1.4598	1.4586	1.4579
Wt. p.c. ...	...	1.4630	1.4620	1.4609	1.4597	1.4588	...
Density—							
Found ...	.8604	.8700	.8807	.8915	.9019	.9095	.9220
Wt. p.c. ...	...	.8709	.8825	.8931	.9034	.9110	...
Mol. p.c. ...	...	.8699	.8805	.8913	.9018	.9098	...
Specific Rotary Power—							
Found ...	29.51°	24.39°	18.80°	13.54°	8.62°	5.06°	0°
Calc. ...	...	24.45°	18.94°	13.83°	8.89°	5.29°	...

The System Cineol-Citral.

Here one of the constituents of the mixture has an open chain. Unfortunately, the refractivities lie too close together for differences to be detected, and both substances are inactive.

The densities show fair agreement when calculated from molar fractions, but apparently other factors are introduced by the wider structural differences.

The citral was from Merck's, and was characterised as follows—

$$\delta_{25} = .8900$$
$$\mu_{25} = 1.4780$$

THE SYSTEM CINEOL–CITRAL.

	Citral.	A.	B.	C	D.	E.	F,	cineol.
				Density—				
Found ..	.8900	.8946	.9001	.9021	.9066	.9096	.9124	.9220
Wt. p.c. ..	...	.8949	.9008	.9030	.9063	.9101	.9127	...
Mol. p.c. ...	...	.8948	.9007	.9026	.9063	.9099	.9126	...
				Concentration cineol—				
Wt. p.c. ...	O	15.24	33.73	40.35	50.98	62.62	70.70	100
Mol. p.c. ...	O	15.07	33.43	40.03	50.65	62.30	70.42	100

The Phellandrene Complex.

We hoped by these methods to obtain from the rotation of a Eucalyptus oil an indication of the amount of phellandrene it contained, and a series of l-phellandrene-cineol mixtures were made up. The preparation of the phellandrene has been elsewhere[1] described, and its constants were—

$$\alpha = -68.35^\circ$$
$$\mu_{25} = .8454$$
$$\delta_{25} = 1.4747$$

The results were rather surprising, for we found that if the measurements be taken immediately after mixing, the density and rotation agree closely with the calculated values, and the refractive index exactly, but the mixtures are unstable, rapidly decreasing in rotation, and increasing in density and refractive index.

This change goes on most rapidly in the presence of light and oxygen, more slowly in the dark, and not at all, as far as we were able to make out, in the absence of oxygen.

Phellandrene itself rapidly changes under similar conditions, attaining equilibrium when its rotation is about +3°. We hope to discuss this matter more fully in a future paper.

THE SYSTEM L-PHELLANDRENE—CINEOL.

	Phellandrene.	A.	B.	C.	D.	E.	cineol.
				Rotation—			
Calc. ...	...	−13.63°	−27.54°	−41.43°	54.75°	−40.76°	...
Obs. 20 hrs.	−68.35°	−12.90°	−25.15°	39.85°	−52.50°	−40.06°	0°
Obs. 48hrs.	...	−12.60°	−21.63°	36.75°	−46.82°	...	...
				Refractive Index—			
Calc. ...	...	1.4627	1.4659	1.4688	1.4719	1.4688	...
Obs. 1 hr....	1.4747	1.4628	1.4659	1.4688	1.4719	1.4688	1.4579
Obs. 44 hrs.	...	1.4631	1.4678	1.4699	1.4734	...	...
				Density—			
Calc. ...	...	.8980	.8845	.8714	.8585	.8719	...
Obs. 1 hr.	...	.8986	.8858	.8728	.8595	.8726	.9202
Obs. 44 hrs.	...	.9018	.8956	.8776	.8678	.8764	...
Concentration. ...	100	19.94	40.30	60.62	80.10	59.64	0

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[1] R. Barry Drew. Australian Association for the Advancement of Science. Report 1913.

Summary.

Simple mixtures of two terpene compounds follow the "Mixture Law" quite closely. The divergences, at any time small, are eliminated by the use of the "Molar Fraction Formula."

For such mixtures the proportions of the constituents can be calculated from the properties of the mixture, but where one constituent is unstable, as in phellandrene oils, such deductions are unreliable.

These measurements were made in the research laboratories of the University of Melbourne, for the use of which we have to thank Professor Masson.

Our thanks are also due to Professor Osborne for the use of his polarimeter, and especially to Mr. H. G. Smith for his generous gift of pinene eucalyptus oils.

PART II.—*The Physical Constants of some Terpenes and oxygenated derivatives thereof, and their variation with temperature.*

BY

E. IVAN ROSENBLUM, M.Sc.

(Communicated by W. Heber Green, D.Sc.).

[Read 9th July, 1914).

Some measurements which had been made in the course of the last paper, and the fact that he had on hand samples of a number of terpenes prepared for that research, led one of the authors to make a series of measurements on the influence of temperature change on the three chief physical constants of terpenes—Density, Refractive Index, and Rotation.

The terpenes employed are, in the main, those whose purification has been described in the joint paper; the others were as supplied by Merck and Kahlbaum, and, with two exceptions, their purity as indicated by their constants and by the usual tests was such as to render it unnecessary to submit them to the somewhat uncertain processes involved in further purification.

The density and refractive index of the terpineol indicate that it is mainly the isomer of M. Pt. 35°–36° C., while the high density and diminished rotation of the d-limonene point to some modification having occurred since it was originally prepared by Kahlbaum.

Although the uncertain purity which is inherent to the terpenes renders these results less valuable from the point of view of physico-chemical theory, they may none the less be regarded as standards by workers in the fascinating field of Essential Oils.

Substance.	Source.	Constants at 20°C.		
		δ	n	α
l-phellandrene	Eucalyptus dives oil	.8551	1.4783	−65.11°
d-pinene	E. dextropinea oil	.8682	1.4659	+25.14°
l-pinene	E. laevopinea oil	.8668	1.4665	−39.81°
pinene	American turpentine	.8603	1.4690	+1.0°
d-limonene	Kahlbaum	.8922	1.4814	+81.95°
cineol	Bosisto, Melbourne	.9239	1.4598	±0.00°
eugenol	Merck	1.0667	1.5415	−0.03°
safrol	Merck	1.1003	1.5385	±0.00°
terpineol	Merck	.9354	1.4835	+0.04°
citral	Merck	.8912	1.4889	±0.00°

(1) The Density.

The densities were measured at ten degree intervals between 10° and 60° by means of a pyknometer holding about 6 c.c., and a bath, which could be maintained at any required temperature, while a measurement was in progress. Incidental errors due to expansion of the glass of the pyknometer, etc., were eliminated by taking a series of pyknometer values for distilled water over the temperature range, calculating the specific gravity from these, and then deriving the density as referred to water at 4° C. from the tables of the density of water.

These densities at ten-degree intervals are shown in the accompanying table.

It will be observed that, while the coefficients of expansion are in all cases close together, they fell into two groups, the oxygenated substances cineol, safrol and eugenol expanding to a greater degree than the hydrocarbons.

Citral, the only straight chain terpene, and terpineol, are exceptional. The relation of temperature to density is strictly linear except in the case of the ever-exceptional l-phellandrene, where a slight divergence is shown.

THE DENSITIES.

Substance.	10°	20°	30°	40°	50°	60°	Coeff.
l-phellandrene	.8635	.8551	.8469	.8387	.8306	.8224	.000826
d-pinene	.8763	.8682	.8602	.8522	.8442	.8361	807
l-pinene	.8750	.8668	.8586	.8504	.8422	.8340	821
pinene	.8685	.8603	.8521	.8439	.8356	.8274	822
d-limonene	.9004	.8922	.8840	.8759	.8679	.8599	811
cineol	.9324	.9239	.9153	.9067	.8982	.8896	857
eugenol	1.0754	1.0667	1.0579	1.0492	1.0404	1.0316	876
safrol	1.1090	1.1003	1.0915	1.0828	1.0740	1.0652	876
terpineol	.9432	.9354	.9276	.9198	.9120	.9042	780
citral	.8992	.8912	.8832	.8752	.8671	.8891	800

(2) The Refractive Index.

Of recent papers on the relation between refractive index and temperature the most interesting are those of Falk[1], who found a linear relation for those substances he examined, none of which, however, were terpenes.

In the present research in every case there are found divergences from this simple proportionality, the temperature coefficient increasing with the rise of temperature except in the cases of cineol and of l-pinene, where it decreases, and the divergences being most marked in the results for l-phellandrene.

Like the coefficients of expansion, these temperature coefficients vary only within narrow limits from .000402 for d-pinene to .000480 for l-phellandrene. Since the coefficients for those organic substancs, whose refractive indices are tabulated in Landolt-Bornstein, vary from .0003 to .0008, this magnitude appears to be a constitutional one. The measurements of refractive index between 10° and 60° are tabulated in the table. They were obtained in a Zeiss refractometer, fitted with a constant temperature device, which ensured constancy to at least .1°.

Three formulae have been suggested for calculating the refractive power—

$$(1)\ n-1/d \quad (2)\ n^2-1/d \ \text{ and } \ (3)\ n^2-1/(n^2+2)d$$

and Falk found that n^2-1/d gave values that decreased as the temperature rose, $n^2-1/(n^2+2d)$ values that increased, while, when $n-1/d$ was used for the calculation, they increased in some cases and decreased in others.

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[1] J. Amer. Chem. Soc., 1909, 31, 86, 806.
Zeit. Physik. Chem., 1913, 82, 504.

This has been confirmed for the terpenes used in the present research, and since the $n-1/d$ figures approach more closely to constancy than those based on the other two formulæ, they have been adopted for comparing the molecular refractive powers.

The constants are calculated by the three formulæ for cineol, l-phellandrene and l-pinene are shown in a table, and the values of $n-1/d \times M$ are shown for all the substances, plotted against the temperatures.

These curves do not show much agreement with one another, the greatest deviations being, as usual, shown by l-phellandrene; but it will be seen that the influence of temperature, though small, is regular, and gives smooth curves.

Eisenlohr[1] has recently obtained as accurately as possible a series

REFRACTIVE INDICES.

Substance.	10°	20°	30°	40°	50°	60°		Average coeff.
l-phellandrene	1.4822	1.4783	1.4742	1.4695	1.4642	1.4582	...	.000480
d-pinene ...	1.4698	1.4659	1.4619	1.4578	1.4537	1.4497	...	.000402
l-pinene ...	1.4713	1.4665	1.4617	1.4570	1.4525	1.4481	...	.000464
pinene ...	1.4734	1.4690	1.4645	1.4598	1.4549	1.4499	...	.000470
d-limonene ...	1.4857	1.4814	1.4769	1.4723	1.4677	1.4630	...	.000454
cineol ...	1.4648	1.4598	1.4550	1.4505	1.4462	1.4420	...	.000456
eugenol ...	1.5455	1.5415	1.5374	1.5329	1.5282	1.5236	...	.0004
safrol ...	1.5425	1.5385	1.5343	1.5300	1.5252	1.5205	...	.000440
terpineol ...	1.4878	1.4835	1.4792	1.4748	1.4706	1.4664	...	.000428
citral ...	1.4929	1.4889	1.4848	1.4802	1.4752	1.4700	...	.000458

REFRACTIVE POWERS BY VARIOUS FORMULAE.

l-phellandrene.					*l-pinene.*			
t°	n^2-1/d	$n-1/d$	$n^2-1/(n^2+2)d$		t°	$n^2\ 1/d$	$n-1/d$	$n_2-1/(n^2+2)d$
10	13868	5584	3302	...	10	13321	5386	3198
20	13851	5593	3312	...	20	13280	5382	3199
30	13849	5598	3323	...	30	13234	5378	3199
40	13827	5597	3324	...	40	13206	5374	3203
50	13770	5588	3318	...	50	13178	5372	3206
60	13696	5571	3319	...	60	13152	5372	3210

Cineol.					*Citral.*			
t°	n^2-1/d	$n-1/d$	$n^2-1/(n^2+2)d$		t°	$n^2\ 1/d$	$n\ 1/d$	$n^2-1/(n_2-2)d$
10	12290	4985	2964	...	10	13663	5482	3231
20	12242	4976	2963	...	20	13653	5485	3238
30	12205	4971	2964	...	30	13639	5488	3244
40	12175	4968	2967	...	40	13605	5487	3247
50	12150	4968	2970	...	50	13565	5481	3248
60	12135	4967	2976	...	60	13515	5472	3249

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[1] Zeit. Physik. Chem., 1911, 75, 585.

Molecular Refractive Power $n - 1/d \,.\, M$

Substance.	10°	20°	30°	40°	50°	60°
l-phellandrene ...	75.94	76.06	76.13	76.12	76.00	75.77
d-pinene	72.92	72.96	73.03	73.08	73.12	73.16
l-pinene	73.24	73.18	73.14	73.08	73.06	73.05
pinene	74.14	74.15	74.14	74.11	74.05	73.96
d-limonene	73.36	73.38	73.37	73.33	73.29	73.23
cineol	76.76	76.62	76.54	76.50	76.49	76.48
eugenol	83.20	83.26	83.32	83.30	83.26	83.23
safrol	79.26	79.29	79.32	79.30	79.24	79.18
terpineol	79.66	79.61	79.57	79.52	79.48	79.44
citral	83.32	83.37	83.42	83.40	83.31	83.18

Molecular Refractions at 20°

a. Found [$n^2 - 1/(n^2 + 2)d \,.\, M$ formula]
b. Calculated from Atomic Refractions[1]

Substance.	*a.*	*b.*
l-phellandrene	45.05	45.25
d-pinene	43.37	43.51
l-pinene	43.48	43.51
pinene	44.03	43.51
d-limonene	43.42	45.25
cineol	45.63	45.62
eugenol	48.35	47.37
safrol	46.08	45.40
terpineol	46.45	45.04
citral	49.22	46.78

of atomic refractions, and these have been used to calculate the theoretical molecular refractions. As will be seen, these are in excellent agreement with the experimental values in some cases, but in others, as in that of citral, where the constants of the sample showed it to be of quite satisfactory purity, the large divergence is difficult to account for. In the cases of eugenol, safrol, and terpineol, it may be due in part to the unknown influence of ring formation.

The value for phellandrene lends some support to Wallach's formula for that terpene, in that it indicates two double bonds.

(3) The Rotation.

Considerable attention has been devoted to the influence of temperature on rotation, and from the work of a number of chemists it appears that the rotation of solids dissolved in non-active sol-

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[1] Eisenlohr. Zeit. Physik. Chem., 1911, 75, 485.

vents increases when the temperature rises, while that of optically active liquids decreases.

Guye and Aston[1] examined some fifty organic liquids, and found that in all cases except that of amyl alcohol the rotatory power diminished with rise of temperature. This exceptional case they explained by the dissociation of previously associated molecules.

The rotations of the only four terpenes which were optically active were measured over a range of from 20° to 60° by means of a Pülfrich polarimeter, fitted with a device for varying the temperature of the tube by means of a bath, and the experimental values are shown in the accompanying table, while the molecular rotatory powers – $a/l.1/d.\mathrm{M}$ – have also been calculated and plotted against the temperature.

The rotations of d- and l-pinene are little affected by temperature change, but slowly decrease as the temperature rises. That of d-limonene falls 0.134° for every degree rise of temperature, while phellandrene again shows its abnormal character by a marked increase of rotation.

In every one of its physical properties then, the curious nature of this terpene, as obtained from the oil of Eucalyptus dives, is expressed. It appears as if it must either be a mixture of two terpenes inseparable by distillation, whose equilibrium is upset by temperature change, or, as seems more probable, the molecules may be associated at the lower temperatures, as in the case of amyl alcohol.

Further work may shed more light on this interesting terpene.

ROTATION.

t°	l-phellandrene.	d-pinene.	d-limonene.	l-pinene.
15°	...	...	...	–40.01°
20°	–65.11°	+25.11°	+81.92°	–39.86°
25°	–65.55°	+25.09°	+81.44°	–39.63°
30°	–66.08°	+25.05°	+80.74°	–39.46°
40°	–67.02°	+24.92°	+79.19°	–39.09°
50°	–67.93°	+24.78°	+77.66°	–38.76°
60°	–69.02°	+24.62°	+76.49°	–38.44°
70°	–70.00°	...	+74.85°	...

MOLECULAR ROTATIONS $\frac{a}{l} \cdot \frac{1}{d} \cdot \mathrm{M}$

Substance.	20°	30°	40°	50°	60°
l-phellandrene ...	103.56	106.12	108.73	111.34	114.08
d-pinene	39.38	39.54	39.72	39.90	40.08
l-pinene	62.42	62.52	62.58	62.63	62.69
d-limonene ...	124.92	124.33	123.48	122.43	121.30

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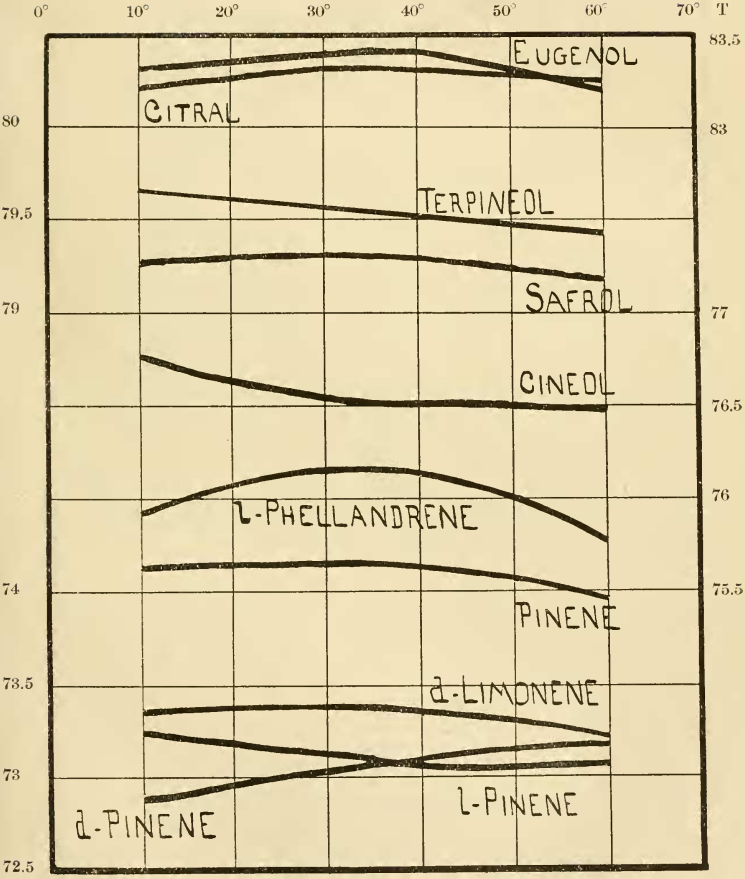
[1] Compt. Rend., 1897, 124, 194-197.
Compt. Rend., 1897, 125, 819-821.

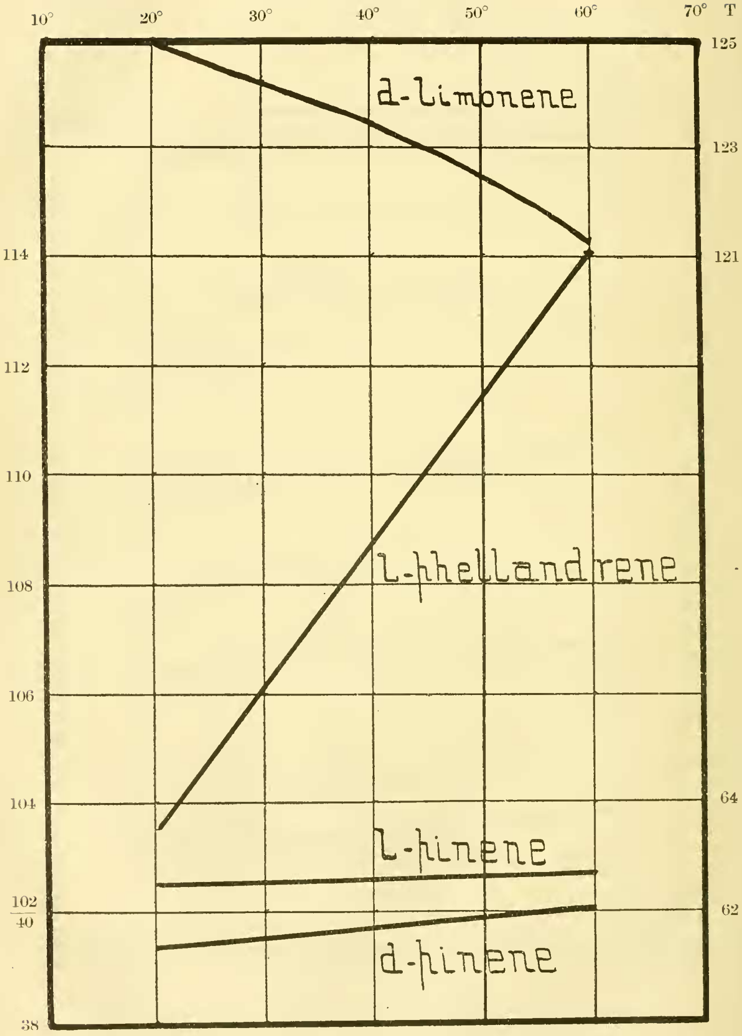
I.

MOLECULAR REFRACTIVE POWER $\frac{M(n-1)}{d}$



II.

Molecular Rotatory Power.



COEFFICIENTS.

Substance.	Density.	Refr. Index.	Rotation.
l-phellandrene ...	.000826	.000480	+.097
d-pinene	807	402	–.013
l-pinene	821	464	–.034
pinene	822	470	...
d-limonene	811	454	–.132
cineol	857	456	...
eugenol	876	458	...
safrol	876	440	...
terpineol	780	428	...
citral	802	458	...

Summary.

1. The influence of temperature change on the density, refractive index, and rotation of a number of terpenes and allied substances has been studied.

2. In the cases of density and refractive index the temperature coefficients all lie close together, while the divergences from a linear relation are slight.

3. Laevo-phellandrene, as obtained from the oil of Eucalyptus dives, is in all its relations somewhat abnormal, and the suggestion is made that it may form associated molecules at the lower temperatures.

The thanks of the author are due to Dr. Heber Green for the interest he has shown in this research.